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(54) **Antibiotic zeolite.**

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PATENT ABSTRACTS OF JAPAN

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Patent Abstract of Japan vol. 10, no. 28 (C-326)(2085) 4. Febr. 1986

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Patent Abstract of Japan vol. 10, no. 328 (C-383) (2384) 7. Nov. 1986

Patent Abstract of Japan vol. 5, no. 200 (C-84) (872) 18. Dec. 1981

Description

Field of the Invention

The present invention relates to an antibiotic zeolite and an antibiotic resin composition containing the zeolite and more particularly to an antibiotic zeolite which does not cause discoloration with time.

Description of the Prior Art

Heretofore, there have been known such inorganic antibiotics as silver-supporting active carbon as disclosed in Japanese Patent Un-examined Publication No. 49-61950 and such organic antibacterial or antifungus agents as N-(fluorodichloromethylthio)-phthalimide.

However, in the former (inorganic antibiotics), silver ions are rapidly leached out therefrom and, therefore, it is difficult to attain a sustained antibiotic effect.

On the other hand, among the latter (organic antibacterial or antifungus agents), some of them have no antibacterial effect depending on the kinds of bacteria or mould (in other words, these being inferior in general-purpose with respect to the kinds of bacteria or mould). Further even those having heat resistance sometimes cause decomposition or evaporation during kneading them into a resin at a temperature of 150 to 300 °C. This leads to the reduction of antibacterial effect.

For the purpose of eliminating the aforementioned disadvantages associated with these conventional antibiotics, there have been developed so-called antibiotic zeolites which comprise an antibiotic component supported on zeolite (see, for instance, Japanese Patent Published for Opposition No. 61-22977 and Japanese Patent Un-examined Publication No. 60-181002).

The aforesaid antibiotic zeolite is certainly an excellent antibitic agent which exhibits a sustained antibiotic action when left to stand in water or in the air and does not cause change of properties during kneading it with a resin. However, such an antibiotic zeolite suffers from a disadvantage that it gradually causes discoloration in the course of time. This discoloration exerts no influence on the antibiotic effect of the antibiotic zeolite and, therefore, the antibiotic zeolite is still an excellent antibiotic agent. However goods in which such an antibiotic zeolite is incorporated sometimes causes discoloration. This leads to remarkable reduction of their commercial value depending on the kinds thereof.

In Patent Abstracts of Japan, Vol. 5, No. 200 (C-84) (872) 18 December 1981, a stabilizer for halogen containing resins is disclosed, the stabilizer comprising as an effective ingredient crystalline zeolite containing Mg, Ba, Ca, Sr, Zn, Cd, Mn, Pb or Sn.

SUMMARY OF THE INVENTION

An object of the present invention is to provide an antibiotic zeolite which does not cause discoloration with time and which exhibits an excellent antibiotic effect as high as that of the conventional antibiotic zeolites.

Another object of the present invention is to provide an antibiotic resin composition comprising the antibiotic zeolite and a resin which does not cause discoloration with time.

The present invention relates to an antibiotic zeolite in which all or a part of ion-exchangeable ions in a zeolite are replaced with silver and ammonium ions.

Further the present invention relates to an antibiotic resin composition comprising resin and an antibiotic zeolite in which all or a part of ion-exchangeable ions in zeolite are replaced with silver and ammonium ions.

BRIEF DESCRIPTION OF THE DRAWINGS

Figs. 1 to 7 show color change with the passage of time of Samples of resins into which the antibiotic zeolites of the invention is incorporated by kneading.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The present invention will hereunder be explained in more detail.

In the antibiotic zeolite of the present invention, either natural zeolites or synthetic zeolites may be used as "zeolite" component. Zeolite is in general aluminosilicate having a three dimensional skeletal structure and represented by the general formula: $XM_{2/n}O\text{-}Al_2O_3\text{-}YSiO_2\text{-}ZH_2O$. In the general formula, M represents

an ion-exchangeable ion and in general a monovalent or divalent metal ion, n represents atomic valency of the (metal) ion, X and Y represent coeficients of metal oxide and silica respectively, and Z represents the number of water of crystallization. Examples of such zeolites include A-type zeolites, X-type zeolites, Y-type zeolites, T-type zeolites, high-silica zeolites, sodalite, mordenite, analcite, clinoptilolite, chabazite and erionite. However, the present invention is not restricted to these specific examples. The ion-exchange capacities of these exemplified zeolite are as follows: A-type zeolite = 7 meq/g; X-type zeolite = 6.4 meq/g; Y-type zeolite = 5 meq/g; T-type zeolite = 3.4 meq/g; sodalite = 11.5 meq/g; mordenite = 2.6 meq/g; analcite = 5 meq/g; clinoptilolite = 2.6 meq/g; chabazite = 5 meq/g; and erionite = 3.8 meq/g. Thus, all the zeolites listed above have ion-exchange capacity sufficient to undergo ion-exchange with ammonium and antibiotic metal ions.

In the antibiotic zeolite of the present invention, ion-exchangeable ions present in zeolite, such as sodium ions, calcium ions, potassium ions and iron ions are completely or partially replaced with ammonium and silver ions. Examples of the antibiotic metal ions which may be further comprised therein include ions of copper, zinc, mercury, tin, lead, bismuth, cadmium, chromium and thallium. Preferably the antibiotic metal ions further comprised therein are copper or zinc ions. From the viewpoint of the antibiotic effect, in general the silver ions are preferably contained in the zeolite in the range of from 0.1 to 15 % of the zeolite. In the present invention, it is preferable that the zeolite contains 0.1 to 15 % of silver ions and 0.1 to 8 % of copper or zinc ions. Although ammonium ion can be contained in the zeolite 20 % or less of the zeolite, it is desirable to limit the content of ammonium ions in the zeolite to a range of from 0.5 to 15%, prerferably 1.5 to 5% from the viewpoint of imparting an excellent antibiotic action thereto. In this connection, the term "%" herein means "% by weight" on the basis of the weight dried at 110 °C.

Methods for preparing the antibiotic zeolite according to the present invention will hereunder be explained.

The antibiotic zeolite of the present invention may be obtained by bringing a zeolite into contact with a previously prepared aqueous mixed solution containing ammonium ions and silver ions and, optionally, antibiotic metal ions such as copper and zinc ions to cause ion-exchange between ion-exchangeable ions in the zeolite and the aforesaid ions. The contact between these ions may be carried out according to a batch technique or a continuous technique (such as a column method) at a temperature of from 10 to 70 °C, preferably from 40 to 60 °C, for 3 to 24 hours, preferably 10 to 24 hours. In this respect, the pH value of the aqueous mixed solution is adjusted to 3 to 10, preferably 5 to 7 in view of preventing the silver oxide and the like from causing deposition on the surface of the zeolite or within the pores thereof. In addition, each of the ions are in general used in the form of a salt to prepare the aqueous mixed solution. For instance, there may be mentioned such an ammonium ion source as ammonium nitrate, ammonium sulfate and ammonium acetate; such a silver ion source as silver nitrate, silver sulfate, silver perchlorate, silver acetate, and diamine silver nitrate; such a copper ion source as copper(II) nitrate, copper sulfate, copper perchlorate, copper acetate, tetracyan copper potassium; such a zinc ion source as zinc(II) nitrate, zinc sulfate, zinc perchlroate, zinc acetate and zinc thiocyanate; such a mercury ion source as mercury perchlorate, mercury nitrate and mercury acetate; such a tin ion source as tin sulfate; such a lead ion source as lead sulfate and lead nitrate; such a bismuth ion source as bismuth chloride and bismuth iodide; such a cadmium ion source as cadmium perchlorate, cadmium sulfate, cadmium nitrate and cadmium acetate; such a chromium ion source as chromium perchlorate, chromium sulfate, chromium ammonium sulfate and chromium acetate; and such a thallium ion source as thallium perchlorate, thallium sulfate, thallium nitrate and thallium acetate.

The content of the ions such as ammonium ions in the zeolite may properly be controlled by adjusting the concentration of each ion species (or salt) in the aforesaid aqueous mixed solution. For example, if the antibiotic zeolite of the invention comprises ammonium and silver ions, the antibiotic zeolite having an ammonium ion content of 0.5 to 5% and a silver ion content of 0.1 to 5% can properly be obtained by bringing a zeolite into contact with an aqueous mixed solution having an ammonium ion concentration of 0.2 M/l to 2.5 M/l and a silver ion concentration of 0.002 M/l to 0.15 M/l. Moreover, if the antibiotic zeolite further comprises copper ions and zinc ions, the antibiotic zeolite having a copper ion content of 0.1 to 8% and a zinc ion content of 0.1 to 8% can properly be obtained by employing an aqueous mixed solution containing 0.1 M/l to 0.85 M/l of copper ions and 0.15 M/l to 1.2 M/l of zinc ions in addition to the aforementioned amounts of ammonium ions and silver ions.

Alternatively, the antibiotic zeolite according to the present invention may also be prepared by using separate aqueous solutions each containing single different ion species (or salt) and bringing a zeolite into contact with each solution one by one to cause ion-exchange there between. The concentration of each ion species in a specific solution can be determined in accordance with the concentrations of these ion species in the aforementioned aqueous mixed solution.

After completion of the ion-exchange, the zeolite thus treated is washed with water sufficiently followed by drying. The zeolite is preferably dried at a temperature of 105 to 115°C under normal pressure or at a temperature of 70 to 90°C under a reduced pressure (1 to 30 torr).

The antibiotic properties of the antibiotic zeolite of the present invention thus prepared may be estimated by determining the minimum growth inhibitory concentration (MIC) with respect to a variety of general bacteria, eumycetes and yeast.

In such a test, the bacteria listed below may be employed:
Bacillus cereus var mycoides, ATCC 11778
Escherichia coli, IFO 3301
Pseudomonas aeruginosa, IIDP-1
Staphylococcus aureus, ATCC 6538P
Streptococcus faecalis, RATCC 8043
Aspergillus niger, IFO 4407
Aureobasiduim pullulans, IFO 6353
Chaetomium globosum, ATCC (6205
Gliocladium virens, IFO 6355
Penicillum funiculosum, IFO 6345
Candida albicans, IFO 1594
Saccharomyces cerevisiae, IFO 1950

The test for determining MIC can be carried out by smearing a solution containing bacteria for innoculation to a plate culture medium to which a test sample of the antibiotic zeolite is added in any concentration and then culturing it. The MIC is defined as a minimum concentration thereof required for inhibiting the growth of each bacteria.

According to the present invention, an antibiotic resin composition is provided. The resin composition comprises the aforementioned antibiotic zeolite and resin.

Examples of the resin include a thermoplastic or thermosetting resin such as polyethylene, polypropylene, polyvinyl chloride, ABS resin, nylons, polyesters, polyvinylidene chloride, polyamides, polystyrene, polyacetals, polyvinyl alcohol, polycarbonate, acrylic resins, fluoroplastics, polyurethane elastomer, phenolic resins, urea resins, melamine resins, unsaturated polyester resins, epoxy resins, urethane resins, rayon, cuprammonium rayon, acetates, triacetates, vinylidene, natural or synthetic rubbers.

The resin composition is prepared by incorporating the antibiotic zeolite into the resin by means of kneading it with the zeolite or coating the antibiotic zeolite on the surface of such a resin in order to impart antibiotic, antifungus and anti-algal properties to each of these plastics. In order to provide antibacterial, antifungus and antialgal properties to a resin composition, the content of the antibiotic zeolite suitably ranges from 0.05 to 80 wt%, preferably 0.1 to 80 wt%. MIC of the antibiotic resin composition can be determined by the similar method to thoes of the antibiotic zeolite per se. Further, from the viewpoint of prevention of substantial discoloration of a resin composition containing the antibiotic zeolite of the present invention, the content of the antibiotic zeolite preferably ranges from 0.1 to 3 wt%.

The antibiotic zeolite according to the present invention may be applied to a variety of fields.

For example, in the field of water systems, the antibiotic zeolite of the present invention may be used as anti-algal agent in water cleaner, water of a cooling tour, and a variety of cooling water, or it may be used as an agent for prolonging life of cut flowers.

In the field of paints, the antibiotic zeolite of the present invention can impart antibiotic, antifungus and anti-algal properties to coated films by directly mixing the zeolite with various kinds of paints such as lyophilic paints, lacquer, varnish, and alkyl resin type, aminoalkyd resin type, vinyl resin type, acrylic resin type, epoxy resin type, urethane resin type, water type, powder type, chlorinated rubber type, phenolic paints; or by coating the zeolite on the surface of the coated films. In the field of construction, the antibiotic zeolite of the invention may impart antibiotic, antifungus and anti-algal properties to various parts for construction such as materials for joint and materials for wall and tile by admixing the zeolite with materials for parts for construction or applying the zeolite to the surface of such a material for construction.

In the field of paper making, the antibiotic zeolite of the invention may be incorporated into various paper materials such as wet tissue paper, paper packaging materials,corrugated boards, a sheet of paper, paper for maintaining freshness by papermaking from a material therefor together with the zeolite; or by coating the resultant paper with the zeolite for the purpose of imparting antibiotic and antifungus properties to these paper. Moreover, in the field of the papermaking, the antibiotic zeolite may also serve in particular as a slime controlling agent.

The antibiotic zeolite according to the present invention may be used in any fields in which the development and proliferation of microorganisms such as general bacteria, eumycetes and algae must be

suppressed, in addition to the foregoing fields.

The present invention will hereunder be explained in more detail with reference to the following non-limitative working examples.

Example 1 (Method for preparing antibiotic zeolites)

In this Example, the following 11 kinds of zeolites were used: A-type zeolite (Na_2O-Al_2O_3-1.9SiO_2-XH_2O; average particle size = 1.5 microns); X-type zeolite (Na_2O-Al_2O_3-2.3SiO_2-XH_2O; average particle size = 2.5 microns); Y-type zeolite (1.1Na_2O-Al_2O_3-4SiO_2-XH_2O; average particle size = 0.7 microns); natural mordenite (0.10 to 0.06 mm mesh width (150 to 250 mesh)); natural clinoptilolite (0.10 to 0.06 mm (150 to 250 mesh)); chabazite (0.10 to 0.06 mm (150 to 250 mesh)); erionite (0.10 to 0.6 mm (150 to 250 mesh)); T-type zeolite (2 microns); high-silica zeolite (5 microns); sadalite (2 microns): and analcite. As the source of each ion species required for ion-exchange, four kinds of salts: NH_4NO_3, $AgNO_3$, $Cu(NO_3)_2$, $Zn(NO_3)_2$, $Hg(NO_3)_2$, $Sn(NO_3)_2$, $Pb(NO_3)_2$, $Cd(NO_3)_2$ and $Cr(NO_3)_3$ were used.

Tables I-1 and I-2 show the details of the kinds of zeolite, the kinds of salts and their concentration in a mixed aqueous solution used to prepare Samples. Thus, 32 Samples of antibiotic zeolites were obtained.

Each Sample was prepared as follows: 1 kg of each zeolite powder which had been dried under heating at 110°C was added to water to form 1.3 liters of slurry, then the slurry was stirred to degasify, proper amounts of 0.5 N nitric acid solution and water were added thereto to adjust the pH to 5 to 7 and to thus obtain a slurry of a total volume of 1.8 liters. Thereafter, ion-exchange was carried out by adding, to the slurry, 3 liters of a mixed aqueous solution containing desired salts each present in a desired amount to obtain a slurry having a total volume of 4.8 liters and maintaining the slurry at a temperature of 40 to 60°C for 10 to 24 hours while stirring to hold the slurry at an equilibrium state. After the ion-exchange was finished, the zeolite phase was filtered off followed by washing with water until almost no excess silver, copper or zinc ions remained in the zeolite phase. Then, Samples thus prepared were dried under heating at 110°C and thus 32 Samples of the antibiotic zeolites were obtained. The data observed on these antibiotic zeolite Samples No. 1 to No. 32 are summarized in Tables I-1 and I-2.

Table I-1

Sample No.	Kind of zeolite	Content in the zeolite (%) NH4	Ag	Cu	Zn	Yield(g)
1	A	1.0	5.0	--	--	960
2	A	1.0	0.5	--	--	955
3	A	1.0	0.05	--	--	958
4	A	0.5	3.0	5.0	--	945
5	X	0.5	5.0	5.0	--	940
6	X	0.5	5.0	8.0	--	943
7	Y	1.0	5.0	--	2.5	910
8	A	1.0	5.0	--	5.0	906
9	Y	1.0	5.0	--	8.0	908
10	Mordenite	3.0	0.5	0.1	--	855
11	ditto	3.0	0.5	0.25	--	861
12	ditto	3.0	0.5	0.5	--	863
13	Clinoptilolite	0.8	0.5	--	0.1	900
14	ditto	0.8	0.5	--	0.25	895
15	ditto	0.8	0.5	--	0.40	901
16	Chabazite	3.0	0.05	0.025	--	880
17	ditto	3.0	0.05	0.05	--	893
18	ditto	3.0	0.05	0.10	--	885
19	Erionite	0.8	0.05	--	0.025	805
20	ditto	0.8	0.05	--	0.05	811
21	ditto	0.8	0.05	--	0.1	808
22	A	1.0	2.0	2.0	2.0	960

Table I-2 (continued)

Sample No.	Composition of mixed aq. solution(M/l) NH_4NO_3	$AgNO_3$	$Cu(NO_3)_2$	$Zn(NO_3)_2$	Solution pH	Ion-E time
1	1.5	0.05	--	--	6.1	10hr
2	1.5	0.015	--	--	5.0	15hr
3	1.5	0.0015	--	--	7.0	20hr
4	1.2	0.10	0.35	--	7.0	12hr
5	1.2	0.15	0.35	--	6.2	15hr
6	1.2	0.15	0.80	--	5.3	18hr
7	3.1	0.15	--	0.18	5.5	15hr
8	3.1	0.15	--	0.40	6.5	10hr
9	3.1	0.15	--	1.00	7.0	24hr
10	2.0	0.015	0.16	--	7.0	10hr
11	2.0	0.015	0.50	--	6.8	15hr
12	2.0	0.015	0.85	--	5.7	20hr
13	1.25	0.015	--	0.30	6.3	24hr
14	1.25	0.015	--	0.60	5.1	18hr
15	1.25	0.015	--	1.20	5.8	12hr
16	2.0	0.002	0.10	--	7.0	12hr
17	2.0	0.002	0.20	--	6.9	12hr
18	2.0	0.002	0.45	--	5.7	12hr
19	1.25	0.002	--	0.15	5.3	15hr
20	1.25	0.002	--	0.40	5.8	15hr
21	1.25	0.002	--	1.00	6.0	15hr
22	3.1	0.068	0.25	0.30	6.0	12hr

Table I-2

Sample No.	Kind of zeolite	Content in the zeolite (%) NH_4	Ag	metal	Yield(g)
23	A	1.0	2.8	3.2 (Hg)	910
24	A	1.1	2.9	3.0 (Sn)	930
25	A	0.8	2.7	4.1 (Pb)	950
26	A	0.7	2.8	4.6 (Cd)	940
27	A	0.6	2.6	4.3 (Cr)	920
28	A	0.7	2.5	2.5 (Cr)	890
29	T	0.7	3.8	--	950
30	high-silica	0.6	2.1	--	960
31	sodalite	1.4	3.2	--	950
32	analcite	1.3	3.1	--	970

Table I-2 (continued)

Sample No.	Composition of mixed aq. solution(M/l) NH_4NO_3	$AgNO_3$	Nitrate of metal	Slurry pH	Ion-Ex time
23	1.2	0.10	0.30	7.0	24hr
24	1.2	0.10	0.5	4.5	24hr
25	1.2	0.10	0.5	6.4	24hr
26	1.2	0.10	0.5	5.8	24hr
27	1.2	0.10	0.5	5.7	24hr
28	1.2	0.10	0.20	5.1	24hr
29	1.5	0.15	--	6.4	24hr
30	1.5	0.30	--	6.7	24hr
31	1.2	0.10	--	6.1	24hr
32	1.2	0.10	--	6.2	24hr

Example 2 (Test on Antibiotic Action)

The antibiotic action was estimated as follows:

The antibiotic action was determined on the following three strains: Aspergillus niger IFO 4407 (mould); Candida albicans IFO 1594 (yeast); and Pseudomonas aeruginosa IID P-1 (general bacteria).

As culture medium for proliferation of microorganisms, Mueller-Hinton Broth (Difco) for bacteria; Poteto Dextrose Agar Medium (Sakae Lab.) for mould; and Yeast Morphology Agar (Difco) for yeast were used. On the other hand, as medium for determining sensitivity, Mueller-Hinton Medium (Difco) for bacteria and Saburo Agar Medium (Sakae Lab.) for mould and yeast were used.

Plates for measuring sensitivity were prepared according in the following manner:

Each Sample was stepwise diluted with sterilized purified water to prepare a number of suspensions having different dilutions, each suspension thus prepared was added to the medium for measuring sensitivity, the temperature of which was raised up to temperature of 50 to 60°C after dissolution, in an amount of 1/9 times volumes of the medium followed by sufficiently mixing, dispensing the product into petri dishes and solidifying the medium to form such plates for measuring sensitivity.

Bacteria solutions for inoculation were prepared as follows:

For bacteria: In this case, the bacteria solution was prepared by inoculating a test strain which had been subcultured on a medium for proliferation of bacteria, culturing it and diluting the medium with the same medium for proliferation of bacteria so that the number of bacterial cells was equal to 10^6/ml.

For mould: The bacteria solution for proliferation of mould was prepared by inoculating a test strain which had been subcultured to a medium for proliferation of mould, culturing it and floating the resulting conidium on a sterilized solution of 0.05% polysorbate 80 so that the number of microorganisms was equal to 10^6 /ml.

For yeast: The solution for inoculation was prepared by inoculating a test strain which had been subcultured on a medium for proliferation of yeast, culturing it and floating the resulting cells of yeast on a sterilized physiologic saline so that the number of yeast cells was equal to 10^6/ml.

Cuture of each microorganism was carried out in the following manner:

The bacteria solution for inoculation was smeared on the plate for measuring sensitivity in the form of a line of 2 cm long with a loop of nichrome wire (inner diameter = about 1 mm) followed by culturing it at 37°C for 18 to 20 hours for bacteria, at 25°C for 7 days for mould. After culturing these for a desired time, the minimum growth inhibitory concentration (MIC) was determined as the concentration at which the growth of microorganisms was completely inhibited.

The results observed are summarized in Table II. In Table II, Sample No. 35 is a commertially available silver-supporting active carbon (supporting 1.4% Ag); and Sample No. 36 is a commercially availalbe silver-supporting active carbon (supporting 0.6% Ag).

Moreover, Sample No. 37 is one for thermal resistance test, which was obtained by heating Sample No. 22 prepared in Example 1 at 350°C for 3 hours in an electric furnace.

Sample No. 38 is one containing 3% of Ag and 5% of Zn obtained by subjecting an A-type zeolite to ion-exchange treatment. Sample No.39 is one containing 2% of Ag and 10% of Zn obtained by subjecting an A-type zeolite to ion-exchange treatment. Samples Nos.38 and 39 did not comprise ammonium ions at all.

Table II

Sample No.	Pseudomonas aeruginosa IID P-1	Strains Tested Aspergillus niger IFO 4407	Candida albicans IFO 1594
1	62.5	500	250
2	2000	2000	2000
4	250	250	250
5	250	250	250
6	125	250	250
7	125	500	250
8	125	500	250
9	125	250	250
10	1000	2000	2000
11	2000	2000	2000
12	2000	2000	2000
13	1000	2000	2000
14	2000	2000	2000
15	1000	2000	2000
22	125	500	250
23	62.5	125	125
24	1000	1000	2000
25	1000	>2000	1000
26	500	1000	500
27	1000	>2000	2000
28	125	250	62.5
35	1000	2000	2000
36	1000	2000	2000
37	125	1000	250
38	125	1000	500
39	125	1000	250

Example 3 (Anti-algal Test)

Three aqueous solutions were prepared by adding 1 liter each of water to cylindrical 2-liter volume of containers of glass and then adding a desired amount of each Sample thereto to form a solution containing 2 g of Sample No. 1, a solution containing 2 g of Sample No. 4 and an aqueous solution free from Samples (blank). These solutions were left to stand for 4 months and were visually observed on whether algae was developed or not. In order to prevent, from lowering, the water level due to the evaporation, water was properly replenished to each container. The results thus observed are summarized in Table III below.

Table III

Time elapsed (days)	No. 1	No. 4	Blank
0	-	-	--
15	-	-	mould was develolped in some degree at water surface and the container surface
30	-	-	mould was developed on all the container suface below the water level
45	-	-	mould was also developed in water
60	-	-	
90	-	-	
120	-	-	

-: Development of mold was not observed;
Sample No. 1: A-type; NH_4 1.0%; Ag 5.0%
Sample No. 4: A-type; NH_4 0.5%; Ag 3.0%; Cu 5.0%

Example 4 (Test on the Amount of silver ions Leached Out)

Sample No. 1 (in the form of pellets of 0.32 cm (1/8) and 0.16 cm (1/16)) was charged in a column of pyrex in an amount of 8.1 g and then tap water was passed therethrough and water samples were collected at a time when 10, 50, 100 or 200 liters of water was passed through the column to determine the concentration of silver ions in each water sample. Such procedures were repeated 3 times. The results obtained are listed in Table IV given below.

Table IV

Number of Experiments	Amount of Water Passed through the Column (liter)			
	10	50	100	200
1	3	2	2	1
2	2	2	1	1
3	3	2	1	1
Average	2.7	2	1.3	1

*: The amount of silver ions are expressed as ppb.
Sample No.1: A-type zeolite; NH_4 1.0%; Ag 5.0%
Column Used: 20mm (ID) X 100mm
Flow Rate: 100 ml/min
Temperature: Room Temperature

It was confirmed that the amount of silver ions dissolved in running water was quite low.

Example 5 (Test on Discoloration)

Samples of antibiotic zeolite which had been dried under heating were added to a resin by kneading in an amount of 1 % by weight and the resultant products were injection-moulded (residence time = 2 min) to form Samples (size of pieces = 7.3 cm X 4.4 cm X 2 mm). The resultant Samples were exposed to sunlight in the air. The color of Samples was determined by placing each Sample on a white Kent paper ($L^*a^*b^*$: 93.1; -0.7; -0.5) with Minolta color-color difference meter CR-100 (using D_{65} rays; see Table VI). In this connection, the color of the antibiotic zeolite per se was determined by packing each zeolite in a petri dish of glass (diameter = 150 mm) while vibrating the petri dish so that the height thereof in the dish was 2 cm (the results obtained were listed in Table V). These results are expressed in accordance with $L^*a^*b^*$ colorimetric system (CIF 1976). In addition, the results on L^* in Table VI are shown in the attached Figs. 1 to 7.

(Samples of antibiotic zeolites)

No. 4: A-type; NH_4 0.5%; Ag 3.0%; Cu 5.0%
No. 38: A-type; Ag 3.0%; Cu 5.0%
No. 8: A-type; NH_4 1.0%; Ag 5.0%; Zn 5.0%
No. 39: A-type; Ag 2.0%; Zn 10.0%

(Resins)

Nylon:	Novamid 1010J (manufactured and sold by MITSUBISHI CHEMICAL INDUSTRIES LTD.)
Polypropylene:	J-109G (manufactured and sold by Ube Chemical Industries, Ltd.)
Low Density Polyethylene:	Suntec F-1920 (manufactured and sold by Asahi Chemical Industry Co., Ltd.)
High Density Polyethylene:	Suntec HDS-360 (manufactured and sold by Asahi Industry Co., Ltd.)
Polystyrene:	GH 9600 (manufactured and sold by DAINIPPON INK AND CHEMICALS, INC.)
ABS Resin:	GTR-10 (manufactured and sold by DENKI KAGAKU KOGYO KABUSHIKI KAISHA)
Vinyl Chloride:	B-3050F2 (manufactured and sold by DENKI KAGAKU KOGYO KABUSHIKI KAISHA) (Added DOP 60 Parts)

Table V

Antibiotic Zeolite	L*	a*	b*
No. 4	90.9	-7.3	-7.2
No. 38	91.1	-8.0	-4.7
No. 8	97.3	-1.6	-1.8
No. 39	95.5	-1.8	-5.2

*: Each Sample was previously dried under heating at 110°C.

Table VI

Sample No.	Heating Conditions Before Kneading Temp. (deg. C)	Heating Conditions Before Kneading Time (hr.)	Injection-Molding Temp. (degree C)	L* 0 day	a*	b*
(nylon)						
No.4	280	3	280	64.8	-9.5	-6.8
No.38	280	3	280	60.0	0.7	18.6
No.8	280	3	280	81.9	-2.5	10.0
No.39	280	3	280	53.2	3.8	22.7
blank	--	--	280	78.2	-0.5	3.2
(polypropylene)						
No.4	260	3	260	64.5	-10.6	0.2
No.38	260	3	260	48.3	2.5	28.6
No.8	260	3	260	68.3	-0.8	7.2
No.39	260	3	260	63.8	-0.7	18.1
blank	--	--	260	77.6	-0.4	3.2
(low density polyethylene)						
No.4	220	3	220	65.9	- 6.3	-8.2
No.38	220	3	220	64.4	-7.9	11.4
No.8	220	3	220	73.3	-3.0	7.4
No.39	220	3	220	63.8	-0.6	17.9
blank	--	--	220	70.7	-1.1	3.3
(high density polyethylene)						
No.4	240	3	240	70.9	- 6.1	-6.7
No.38	240	3	240	66.5	-7.1	10.9
No.8	240	3	240	81.6	-0.2	5.5
No.39	240	3	240	68.6	-0.5	13.8
blank	--	--	240	78.5	-1.6	-3.1
(polystyrene)						
No.4	230	3	230	72.7	- 9.9	1.1
No.38	230	3	230	68.6	-5.0	16.2
No.8	230	3	230	81.6	-2.6	11.1
No.39	230	3	230	66.8	-1.5	11.3
blank	--	--	230	85.9	-2.0	-3.4
(ABS resin)						
No.4	250	3	250	61.8	- 3.8	1.5
No.38	250	3	250	48.1	-0.3	2.0
No.8	250	3	250	69.9	-1.9	13.4
No.39	250	3	250	46.9	0.4	3.5
blank	--	--	250	81.0	-4.2	12.3
(vinyl chloride)						
No.4	180	3	180	66.9	- 7.9	-1.2
No.38	180	3	180	68.5	-7.5	-0.8
No.8	180	3	180	73.4	-2.4	7.3
No.39	180	3	180	72.0	-2.2	6.5
blank	--	--	180	74.5	0.2	4.1

Table VI (continued)

Sample No.	10 days L*	a*	b*	30 days L*	a*	b*	60 days L*	a*	b*
(nylon)									
No.4	64.8	-9.4	-5.5	63.0	-9.3	-4.0	61.2	-9.3	-2.1
No.38	52.0	2.4	19.8	48.9	2.7	20.7	45.2	3.2	21.1
No.8	81.6	-2.4	10.5	81.0	-2.2	11.1	80.0	-2.0	12.0
No.39	48.9	4.4	23.1	40.2	4.9	24.8	37.2	5.1	25.5
blank	75.1	0.1	4.2	72.6	0.2	6.5	72.3	0.2	6.7
(polypropylene)									
No.4	64.0	-9.8	1.5	63.5	-8.6	4.3	61.7	-6.4	8.7
No.38	44.0	3.0	29.5	41.2	3.6	30.7	39.1	3.8	31.1
No.8	67.6	-0.7	8.9	66.4	-0.7	11.5	66.2	-0.7	12.1
No.39	56.0	1.5	19.4	52.4	2.1	20.0	51.7	2.6	20.5
blank	74.7	0.1	4.5	73.5	0.4	4.7	73.0	0.5	5.1
(low density polyethylene)									
No.4	64.9	-6.3	-5.3	63.8	-6.3	-2.9	63.2	-6.3	-2.2
No.38	52.8	-3.3	14.5	48.6	-1.8	16.3	46.0	0.2	18.5
No.8	71.9	-4.5	13.1	71.0	-5.0	15.9	70.6	-5.1	18.0
No.39	59.4	1.5	18.8	54.6	2.2	19.6	52.4	2.4	20.4
blank	68.6	1.8	4.6	68.0	2.2	6.0	67.7	2.5	7.1
(high density polyethylene)									
No.4	68.0	-6.1	-3.8	67.2	-6.1	-2.4	66.5	-6.0	-2.0
No.38	55.0	-2.9	13.9	50.5	-1.5	15.5	48.2	0.2	17.7
No.8	80.1	-0.3	8.8	79.2	-0.3	11.5	78.7	-0.3	12.9
No.39	61.2	1.0	15.7	57.2	2.0	17.6	55.6	2.6	18.1
blank	74.0	1.2	1.2	73.1	1.8	2.9	72.8	2.2	3.5
(polystyrene)									
No.4	71.4	-9.5	0	70.8	-8.9	-0.7	69.6	-8.6	-1.3
No.38	58.3	-3.3	8.2	54.5	-1.3	4.8	51.7	0	1.5
No.8	75.7	-1.3	13.4	70.5	-0.9	14.9	68.6	-0.6	15.2
No.39	55.9	-0.2	10.5	50.3	0.8	9.4	47.7	1.0	9.0
blank	80.9	0	-1.2	79.9	0.7	1.5	78.6	1.1	2.5
(ABS resin)									
No.4	56.7	-2.4	2.9	52.2	-1.8	4.9	49.5	-1.6	5.1
No.38	46.4	-0.1	3.1	45.9	0	4.4	45.3	0	4.7
No.8	63.5	1.0	12.9	60.5	-0.8	10.2	59.6	-0.7	8.4
No.39	40.6	0.4	3.5	38.1	0.5	3.5	37.5	0.6	3.4
blank	78.3	-2.5	13.8	78.0	-0.4	14.2	77.0	-0.2	14.5
(vinyl chloride)									
No.4	64.7	-6.6	1.2	62.3	-5.7	4.6	60.8	-5.1	8.7
No.38	36.3	-0.1	4.2	33.5	0.7	10.5	30.1	1.2	15.3
No.8	63.1	0	15.5	55.1	2.3	21.1	53.1	4.1	25.5
No.39	47.0	4.7	20.6	36.1	5.2	25.5	28.6	8.6	35.0
blank	65.9	0.9	6.1	63.2	1.7	9.2	62.8	2.8	12.1

Effects of the Invention

The antibiotic zeolite according to the present invention exhibits an antibiotic action as good as that of the conventional antibiotic zeolite and extremely low change in color as compared with that of the conventional product. Therefore, the antibiotic zeolite of the invention is greatly improved in its properties.

Moreover, the amount of silver leached out therefrom is also very low compared with the conventional ones due to the presence of ammonium ions.

Claims

Claims for the following Contracting States : AT, BE, CH, DE, FR, GB, IT, LI, NL, SE

1. An antibiotic zeolite in which all or a part of ion-exchangeable ions in zeolite are replaced with silver and ammonium ions.

2. An antibiotic zeolite according to claim 1 further comprising at least one ion of metals selected from the group consiting of copper, zinc, mercury, tin, lead, bismuth, cadmium, chromium and thallium.

3. An antibiotic zeolite according to claim 2 wherein the metal ions are copper or zinc ions.

4. An antibiotic zeolite according to anyone of claims 1 to 3 wherein the zeolite is a natural zeolite or a synthetic zeolite

5. An antibiotic zeolite according to any one of claims 1 to 4 wherein the zeolite is selected from the group consisting of A-type zeolites, X-type zeolites, Y-type zeolites, T-type zeolites, high-silica zeolites, sodalite, mordenite, analcite, clinoptilolite, chabazite and erionite.

6. An antibiotic zeolite according to any one of claims 1 to 5 wherein the ammonium ion is contained in the zeolite in the range of from 0.5 to 15 wt%.

7. An antibiotic zeolite accoding to claim 6 wherein the ammonium ion is contained in the zeolite in the range of from 1.5 to 5 wt%.

8. An antibiotic zeolite according to any one of claims 2 to 7 wherein the content of the silver ion ranges from 0.1 to 15 wt%, the content of copper ranges from 0.1 to 8 wt% and the content of zinc ranges from 0.1 to 8 wt%.

9. An antibiotic resin composition comprising resin and an antibiotic zeolite in which all or a part of ion-exchangeable ions in zeolite being replaced with silver and ammonium ions.

10. An antibiotic resin composition according to claim 9 wherein the resin is at least one member selected from the group consisting of polyethylene, polypropylene, polyvinyl chloride, ABS resin, nylons, polyesters, polyvinylidene chloride, polyamides, polystyrene, polyacetals, polyvinyl alcohol, polycarbonate, acrylic resins, fluoroplastics, polyurethane elastomer, phenolic resins, urea resins, melamine resins, unsaturated polyester resins, epoxy resins, urethane resins, rayon, cuprammonium rayon, acetates, triacetates, vinylidene, natural or synthetic rubbers.

11. An antibiotic resin composition according to claim 9 or 10 wherein the content of the antibiotic zeolite ranges from 0.05 to 80 wt%.

12. An antibiotic resin composition according to claim 11 wherein the content of the antibiotic zeolite ranges from 0.1 to 80 wt%.

13. An antibiotic resin composition according to claim 12 wherein the content of the antibiotic zeolite ranges from 0.1 to 3 wt%.

14. An antibiotic resin composition according to any one of claims 9 to 13 further comprising at least one ion of metals selected from the group consisting of copper, zinc, mercury, tin, lead, bismuth, cadmium, chromium and thallium.

15. An antibiotic resin composition according to claim 14 wherein the metal ions are copper or zinc.

16. An antibiotic resin composition according to any one of claims 9 to 15 wherein the ammonium ion is contained in the zeolite in the range of from 0.5 to 15 wt%.

17. An antibiotic resin composition according to claim 15 or 16 wherein the content of silver ion ranges from 0.1 to 15 wt%, the content of copper ranges from 0.1 to 8 wt% and the content of zinc ranges from 0.1 to 8 wt%.

Claims for the following Contracting State : ES

1. A method for preparing an antibiotic zeolite, the method comprising the step of replacing all or part of the ion exchangeable ions in the zeolite with silver and ammonium ions.

2. The method of claim 1 in which the replacing step is performed by preparing a solution containing ammonium ions and silver ions in a desired concentration thereof and contacting the zeolite with the solution in order to allow all or part of the ion exchangeable ions to be replaced with silver and ammonium ions.

3. The method of claim 1 or 2 in which the zeolite is washed and dried after completion of the ion exchange.

4. The method of any one of claims 1 to 3 in which the ion exchange is carried out in a batch technique or a continuous technique.

5. The method of any one of claims 1 to 4 in which the ion exchange is carried out at a temperature of from 10 to 70 °C.

6. The method of any one of claims 2 to 5 in which the pH-value of the solution containing the ammonium and silver ions is adjusted to 3 to 10.

7. The method of any one of claims 1 to 6 further comprising replacing ion exchangeable ions in the zeolite with ions of at least one metal selected from the group consisting of copper, zinc, mercury, tin, lead, bismuth, cadmium, chromium and thallium.

8. The method of any one of claims 1 to 7 in which a natural zeolite or a synthetic zeolite is employed.

9. The method of any one of claims 1 to 8 in which the zeolite is selected from the group consisting of A-type zeolites, X-type zeolites, Y-type zeolites, T-type zeolites, high-silica zeolites, sodalite, mordenite, analcite, clinoptilolite, chabazite and erionite.

10. The method of any one of claims 1 to 9 in which the ammonium ion is introduced into the zeolite in an amount of from 0.5 to 15 wt%.

11. The method of any one of claims 1 to 10 in which the ammonium ion is introduced into the zeolite in an amount of from 1.5 to 5 wt%.

12. The method of any one of claims 7 to 11 in which the silver ion is introduced into the zeolite in an amount of from 0.1 to 15 wt%, the copper ion is introduced in an amount of from 0.1 to 8 wt% and the zinc ion is introduced in an amount of from 0.1 to 8 wt%.

13. The method of any one of claims 7 to 12 in which the step of replacing all or part of the ion exchangeable ions in the zeolite is performed by contacting the zeolite with a mixed solution containing besides ammonium and silver ions ions of at least one metal selected from the group consisting of copper, zinc, mercury, tin, lead, bismuth, cadmium, chromium and thallium.

14. The method of any one of claims 7 to 12 in which the step of replacing all or part of the ion exchangeable ions in the zeolite is performed by contacting the zeolite with separate solutions each containing at least one ion selected from the group consisting of ammonium, silver, copper, zinc, mercury, tin, lead, bismuth, cadmium, chromium and thallium.

15. A method for preparing an antibiotic resin composition comprising the step of incorporating a zeolite in which all or a part of ion exchangeable ions were replaced with silver and ammonium ions into the resin

by means of kneading the resin with the zeolite or coating the zeolite on the surface of the resin.

16. The method of claim 15 in which a resin is employed which is at least one member selected from the group consisting of polyethylene, polypropylene, polyvinyl chloride, ABS resin, nylons, polyesters, polyvinylidene chloride, polyamides, polystyrene, polyacetals, polyvinyl alcohol, polycarbonate, acrylic resins, fluoroplastics, polyurethane elastomer, phenolic resins, urea resins, melamine resins, unsaturated polyester resins, epoxy resins, urethane resins, rayon, cuprammonium rayon, acetates, triacetates, vinylidene, natural or synthetic rubbers.

17. The method of claim 15 or 16 in which the antibiotic zeolite is introduced in an amount of from 0.05 to 80 wt%.

18. The method of any one of claims 15 to 17 in which the antibiotic zeolite is introduced in an amount of 0.1 to 80 wt%.

19. The method of any one of claims 15 to 18 in which the antibiotic zeolite is incorporated in an amount of from 0.1 to 3 wt%.

20. The method of any one of claims 15 to 19 in which a zeolite further comprising ions of at least one metal selected from the group consisting of copper, zinc, mercury, tin, lead, bismuth, cadmium and thallium is incorporated.

21. The method of any one of claims 15 to 20 in which a zeolite containing ammonium ions in an amount of from 0.5 to 15 wt% is incorporated.

22. The method of any one of claims 20 to 21 in which a zeolite containing silver ions in an amount of from 0.1 to 15 wt%, copper ions in an amount of from 0.1 to 8 wt% and zinc ions in an amount of from 0.1 to 8 wt% is incorporated.

23. The method of any one of claims 15 to 22 in which a zeolite is incorporated which was prepared according to the method of any one of claims 1 to 14.

Patentansprüche
Patentansprüche für folgende Vertragsstaaten : AT, BE, CH, DE, FR, GB, IT, LI, NL, SE

1. Ein antibiotischer Zeolith, in dem alle oder ein Teil der Ionen-austauschbaren Ionen im Zeolithen durch Silber- und Ammoniumionen ersetzt sind.

2. Ein antibiotischer Zeolith nach Anspruch 1, der weiterhin mindestens ein Ion von aus der aus Kupfer, Zink, Quecksilber, Zinn, Blei, Wismut, Cadmium, Chrom und Thallium bestehenden Gruppe ausgewählten Metallen enthält.

3. Ein antibiotischer Zeolith nach Anspruch 2, in dem die Metallionen Kupfer- oder Zinkionen sind.

4. Ein antibiotischer Zeolith nach einem der Ansprüche 1 bis 3, bei dem der Zeolith ein natürlicher Zeolith oder ein synthetischer Zeolith ist.

5. Ein antibiotischer Zeolith nach einem der Ansprüche 1 bis 4, bei dem der Zeolith ausgewählt ist aus der Gruppe, die besteht aus Zeolithen vom A-Typ, Zeolithen vom X-Typ, Zeolithen vom Y-Typ, Zeolithen vom T-Typ, siliziumoxidreichen Zeolithen, Sodalith, Mordenit, Analcit, Klinoptilolit, Chabasit und Erionit.

6. Ein antibiotischer Zeolith nach einem der Ansprüche 1 bis 5, bei dem das Ammoniumion in dem Zeolithen im Bereich von 0,5 bis 15 Gew.-% enthalten ist.

7. Ein antibiotischer Zeolith nach Anspruch 6, bei dem das Ammoniumion in dem Zeolithen im Bereich von 1,5 bis 5 Gew.-% enthalten ist.

8. Ein antibiotischer Zeolith nach einem der Ansprüche 2 bis 7, bei dem der Gehalt des Silberions im Bereich von 0,1 bis 15 Gew.-%, der Gehalt des Kupfers im Bereich von 0,1 bis 8 Gew.-% und der Gehalt des Zinks im Bereich von 0,1 bis 8 Gew.-% liegt.

9. Eine antibiotische Harzzusammensetzung, die Harz und einen antibiotischen Zeolithen, in dem alle oder ein Teil der Ionen-austauschbaren Ionen im Zeolithen durch Silber- und Ammoniumionen ersetzt sind, enthält.

10. Eine antibiotische Harzzusammensetzung nach Anspruch 9, bei der das Harz mindestens ein aus der Gruppe ausgewähltes Mitglied ist, welche besteht aus Polyethylen, Polypropylen, Polyvinylchlorid, ABS-Harz, Nylons, Polyestern, Polyvinylidenchlorid, Polyamiden, Polystyrol, Polyacetalen, Polyvinylalkohol, Polycarbonat, Acrylharzen, Fluorkunststoffen, Polyurethanelastomer, Phenolharzen, Harnstoffharzen, Melaminharzen, ungesättigten Polyesterharzen, Expoxyharzen, Urethan-Harzen, Reyon, Kupferammonium-Reyon, Acetaten, Triacetaten, Vinyliden, natürlichen oder synthetischen Gummis.

11. Eine antibiotische Harzzusammensetzung nach Anspruch 9 oder 10, bei der der Gehalt des antibiotischen Zeolithen im Bereich von 0,05 bis 80 Gew.-% liegt.

12. Eine antibiotische Harzzusammensetzung nach Anspruch 11, bei der der Gehalt des antibiotischen Zeolithen im Bereich von 0,1 bis 80 Gew.-% liegt.

13. Eine antibiotische Harzzusammensetzung nach Anspruch 12, bei der der Gehalt des antibiotischen Zeolithen im Bereich von 0,1 bis 3 Gew.-% liegt.

14. Eine antibiotische Harzzusammensetzung nach einem der Ansprüche 9 bis 13, die weiterhin mindestens ein Ion enthält von aus der aus Kupfer, Zink, Quecksilber, Zinn, Blei, Wismut, Cadmium, Chrom und Thallium bestehenden Gruppe ausgewählten Metallen.

15. Eine antibiotische Harzzusammensetzung nach Anspruch 14, bei der die Metallionen Kupfer oder Zink sind.

16. Eine antibiotische Harzzusammensetzung nach einem der Ansprüche 9 bis 15, bei der das Ammoniumion in dem Zeolithen im Bereich von 0,5 bis 15 Gew.-% enthalten ist.

17. Eine antibiotische Harzzusammensetzung nach Anspruch 15 oder 16, bei der der Gehalt an Silberionen im Bereich von 0,1 bis 15 Gew.-%, der Gehalt an Kupfer im Bereich von 0,1 bis 8 Gew.-% und der Gehalt an Zink im Bereich von 0,1 bis 8 Gew.-% liegt.

Patentansprüche für folgenden Vertragsstaat : ES

1. Ein Verfahren zur Herstellung eines antibiotischen Zeolithen, das den Schritt des Ersetzens aller oder eines Teils der Ionen-austauschbaren Ionen in dem Zeolithen durch Silber- und Ammoniumionen aufweist.

2. Das Verfahren nach Anspruch 1, bei dem der Schritt des Ersetzens durchgeführt wird durch Herstellen einer Ammoniumionen und Silberionen in gewünschter Konzentration enthaltenden Lösung und In-Kontakt-Bringen des Zeolithen mit der Lösung, um zu erlauben, daß alle oder ein Teil der Ionen-austauschbaren Ionen durch Silber- und Ammoniumionen ersetzt werden.

3. Das Verfahren nach Anspruch 1 oder 2, bei dem der Zeolith nach Vollendung des Ionenaustauschs gewaschen und getrocknet wird.

4. Das Verfahren nach einem der Ansprüche 1 bis 3, bei dem der Ionenaustausch in einem diskontinuierlichen Verfahren oder einem kontinuierlichen Verfahren durchgeführt wird.

5. Das Verfahren nach einem der Ansprüche 1 bis 4, bei dem der Ionenaustausch bei einer Temperatur von 10 °C bis 70 °C durchgeführt wird.

6. Das Verfahren nach einem der Ansprüche 2 bis 5, bei dem der pH-Wert der die Ammonium- und Silberionen enthaltenden Lösung auf 3 bis 10 eingestellt wird.

7. Das Verfahren nach einem der Ansprüche 1 bis 6, weiterhin aufweisend das Ersetzen von Ionen-austauschbaren Ionen in dem Zeolithen durch Ionen mindestens eines Metalls, das ausgewählt ist aus der aus Kupfer, Zink, Quecksilber, Zinn, Blei, Wismut, Cadmium, Chrom und Thallium bestehenden Gruppe.

8. Das Verfahren nach einem der Ansprüche 1 bis 7, bei dem ein natürlicher Zeolith oder ein synthetischer Zeolith verwendet wird.

9. Das Verfahren nach einem der Ansprüche 1 bis 8, bei dem der Zeolith ausgewählt ist aus der Gruppe, die besteht aus Zeolithen vom A-Typ, Zeolithen vom X-Typ, Zeolithen vom Y-Typ, Zeolithen vom T-Typ, siliziumoxidreichen Zeolithen, Sodalith, Mordenit, Analcit, Klinoptilolit, Chabasit und Erionit.

10. Das Verfahren nach einem der Ansprüche 1 bis 9, bei dem das Ammoniumion in einer Menge von 0,5 bis 15 Gew.-% in den Zeolithen eingeführt wird.

11. Das Verfahren nach einem der Ansprüche 1 bis 10, bei dem das Ammoniumion in einer Menge von 1,5 bis 5 Gew.-% in den Zeolithen eingeführt wird.

12. Das Verfahren nach einem der Ansprüche 7 bis 11, bei dem das Silberion in einer Menge von 0,1 bis 15 Gew.-%, das Kupferion in einer Menge von 0,1 bis 8 Gew.-% und das Zinkion in einer Menge von 0,1 bis 8 Gew.-% in den Zeolithen eingeführt wird.

13. Das Verfahren nach einem der Ansprüche 7 bis 12, bei dem der Schritt des Ersetzens aller oder eines Teils der Ionen-austauschbaren Ionen in dem Zeolithen durchgeführt wird durch In-Kontakt-Bringen des Zeolithen mit einer gemischten Lösung, die außer Ammonium- und Silberionen Ionen mindestens eines Metalls enthält, das ausgewählt ist aus der aus Kupfer, Zink, Quecksilber, Zinn, Blei, Wismut, Cadmium, Chrom und Thallium bestehenden Gruppe.

14. Das Verfahren nach einem der Ansprüche 7 bis 12, bei dem der Schritt des Ersetzens aller oder eines Teils der Ionen-austauschbaren Ionen in dem Zeolithen durchgeführt wird durch In-Kontakt-Bringen des Zeolithen mit getrennten Lösungen, die jeweils mindestens ein Ion enthalten, das ausgewählt ist aus der aus Ammonium, Silber, Kupfer, Zink, Quecksilber, Zinn, Blei, Wismut, Cadmium, Chrom und Thallium bestehenden Gruppe.

15. Ein Verfahren zur Herstellung einer antibiotischen Harzzusammensetzung, aufweisend den Schritt des Inkorporierens eines Zeolithen, in dem alle oder ein Teil der Ionen-austauschbaren Ionen durch Silber- und Ammoniumionen ersetzt wurden, in das Harz mittels Kneten des Harzes mit dem Zeolithen oder Beschichten des Zeolithen auf die Oberfläche des Harzes.

16. Das Verfahren nach Anspruch 15, bei dem ein Harz verwendet wird, das mindestens ein aus der Gruppe ausgewähltes Mitglied ist, die besteht aus Polyethylen, Polypropylen, Polyvinylchlorid, ABS-Harz, Nylons, Polyestern, Polyvinylidenchlorid, Polyamiden, Polystyrol, Polyacetalen, Polyvinylalkohol, Polycarbonat, Acrylharzen, Fluorkunststoffen, Polyurethanelastomer, Phenolharzen, Harnstoffharzen, Melaminharzen, ungesättigten Polyesterharzen, Epoxyharzen, Urethanharzen, Reyon, Kupferammonium-Reyon, Acetaten, Triacetaten, Vinyliden, natürlichen oder synthetischen Gummis.

17. Das Verfahren nach Anspruch 15 oder 16, bei dem der antibiotische Zeolith in einer Menge von 0,05 bis 80 Gew.-% eingeführt wird.

18. Das Verfahren nach einem der Ansprüche 15 bis 17, bei dem der antibiotische Zeolith in einer Menge von 0,1 bis 80 Gew.-% eingeführt wird.

19. Das Verfahren nach einem der Ansprüche 15 bis 18, bei dem der antibiotische Zeolith in einer Menge von 0,1 bis 3 Gew.-% inkorporiert wird.

20. Das Verfahren nach einem der Ansprüche 15 bis 19, bei dem ein Zeolith inkorporiert wird, der weiterhin Ionen mindestens eines Metalls enthält, das ausgewählt ist aus der aus Kupfer, Zink, Quecksilber, Zinn, Blei, Wismut, Cadmium und Thallium bestehenden Gruppe.

21. Das Verfahren nach einem der Ansprüche 15 bis 20, bei dem ein Zeolith inkorporiert wird, der Ammoniumionen in einer Menge von 0,5 bis 15 Gew.-% enthält.

22. Das Verfahren nach einem der Ansprüche 20 bis 21, bei dem ein Zeolith inkorporiert wird, der Silberionen in einer Menge von 0,1 bis 15 Gew.-%, Kupferionen in einer Menge von 0,1 bis 8 Gew.-% und Zinkionen in einer Menge von 0,1 bis 8 Gew.-% enthält.

23. Das Verfahren nach einem der Ansprüche 15 bis 22, bei dem ein Zeolith inkorporiert wird, der nach dem Verfahren nach einem der Ansprüche 1 bis 14 hergestellt wurde.

Revendications
Revendications pour les Etats contractants suivants : AT, BE, CH, DE, FR, GB, IT, LI, NL, SE

1. Une zéolithe antibiotique dans laquelle la totalité ou une partie des ions échangeables ioniquement dans la zéolithe est remplacée par des ions argent et ammonium.

2. Une zéolithe antibiotique selon la revendication 1, comprenant en outre au moins un ion de métal choisi dans le groupe comprenant le cuivre, le zinc, le mercure, l'étain, le plomb, le bismuth, le cadmium, le chrome et le thallium.

3. Une zéolithe antibiotique selon la revendication 2, selon laquelle les ions métalliques comprennent les ions cuivre ou zinc.

4. Une zéolithe antibiotique conformément à l'une quelconque des revendications 1 à 3, selon laquelle la zéolithe et une zéolithe naturelle ou une zéolithe synthétique.

5. Une zéolithe antibiotique conformément à l'une quelconque des revendications 1 à 4 selon laquelle la zéolithe est choisie dans le groupe comprenant les zéolithes du type A, les zéolithes du type X, les zéolithes du type Y, les zéolithes du type T, les zéolithes à teneur élevée en silice, la sodalite, la mordénite, l'analcite, la clinoptilolite, la chabazite et l'érionite.

6. Une zéolithe antibiotique selon l'une quelconque des revendications 1 à 5, selon laquelle l'ion ammonium est contenu dans la zéolithe dans l'intervalle de 0,5 à 15 % en poids.

7. Une zéolithe antibiotique selon la revendication 6, selon laquelle l'ion ammonium est contenu dans la zéolithe dans l'intervalle de 1,5 à 5 % en poids.

8. Une zéolithe antibiotique selon l'une quelconque des revendications 2 à 7, selon laquelle la teneur de l'ion argent est dans l'intervalle de 0,1 à 15 % en poids, la teneur du cuivre est dans l'intervalle de 0,1 à 8% en poids et la teneur en zinc est dans l'intervalle de 0,1 à 8 % en poids.

9. Une composition de résine antibiotique comprenant une résine et une zéolithe antibiotique dans laquelle la totalité ou une partie des ions échangeables ioniquement dans la zéolithe est remplacée par des ions argent et ammonium.

10. Une composition de résine antibiotique selon la revendication 9, selon laquelle la résine est au moins un membre choisi dans le groupe comprenant les suivants : polyéthylène, polypropylène, chlorure de polyvinyle, résine ABS, nylons, polyesters, chlorure de polyvinylidène, polyamides, polystyrène, polyacétals, alcool polyvinylique, polycarbonate, résines acryliques, fluoroplastiques, élastomère de polyuréthanne, résines phénoliques, résines d'urées, résines de mélamine, résines de polyesters insaturés, résines époxy, résines d'uréthanne, rayonne, rayonne cuproammoniacale, acétates, triacétates, vinylidène, caoutchoucs naturels ou synthétiques.

11. Une composition de résine antibiotique conformément à la revendication 9 ou 10, selon laquelle la teneur de la zéolithe antibiotique est dans l'intervalle de 0,05 à 80 %.

12. Une composition de résine antibiotique conformément à la revendication 11, selon laquelle la teneur en zéolithe antibiotique est dans l'intervalle de 0,1 à 80 %.

13. Une composition de résine antibiotique conformément à la revendication 12, selon laquelle la teneur en zéolithe antibiotique est dans l'intervalle de 0,1 à 3 % en poids.

14. Une composition de résine antibiotique conformément à l'une quelconque des revendications 9 à 13, comprenant en outre au moins un ion de métaux choisi dans le groupe comprenant les suivants : cuivre, zinc, mercure, étain, plomb, bismuth, cadmium, chrome et thallium.

15. Une composition de résine antibiotique selon la revendication 14, selon laquelle les ions métalliques comprennent le cuivre ou le zinc.

16. Une composition de résine antibiotique selon l'une quelconque des revendications 9 à 15, selon laquelle l'ion ammonium est contenu dans la zéolithe dans l'intervalle de 0,5 à 15 % en poids.

17. Une composition de résine antibiotique selon la revendication 15 ou 16, selon laquelle la teneur en ion argent est dans l'intervalle de 0,1 à 15 % en poids, la teneur en cuivre est dans l'intervalle de 0,1 à 8 % en poids et la teneur en zinc est dans l'intervalle de 0,1 à 8 % en poids.

Revendications pour l'Etat contractant suivant : ES

1. Une méthode de préparation d'une zéolithe antibiotique, la méthode comprenant l'étape de remplacement de la totalité ou d'une partie des ions échangeable ioniquement dans la zéolithe par des ions argent et ammonium.

2. La méthode selon la revendication 1, selon laquelle l'étape de remplacement est conduite en préparant une solution contenant les ions ammonium et des ions argent à une concentration désirée de ces ions et en mettant en contact la zéolithe avec la solution pour permettre à la totalité ou à une partie des ions échangeables ioniquement d'être remplacée par les ions argent et ammonium.

3. La méthode selon la revendication 1 ou 2, selon laquelle la zéolithe est lavée et séchée à la fin de l'échange d'ions.

4. La méthode selon l'une quelconque des revendications 1 à 3, selon laquelle l'échange d'ions est conduit selon une technique en discontinu ou selon une technique en continu.

5. La méthode selon l'une quelconque des revendications 1 à 4, selon laquelle l'échange d'ions est conduit à une température de 10 à 70 °C.

6. La méthode selon l'une quelconque des revendications 2 à 5, selon laquelle la valeur de pH de la solution contenant les ions ammonium et argent est ajustée à 3 à 10.

7. La méthode selon l'une quelconque des revendications 1 à 6 comprenant en outre le remplacement des ions échangeables ioniquement dans la zéolithe par des ions d'au moins un métal choisi dans le groupe comprenant les suivants : cuivre, zinc, mercure, étain, plomb, bismuth, cadmium, chrome et thallium.

8. La méthode selon l'une quelconque des revendications 1 à 7, selon laquelle une zéolithe naturelle ou une zéolithe synthétique est employée.

9. La méthode selon l'une quelconque des revendications 1 à 8, selon laquelle la zéolithe est choisie dans le groupe comprenant les suivants : zéolithes du type A, zéolithes du type X, zéolithes du type Y, zéolithes du type T, zéolithes à haute teneur en silice, sodalite, mordénite, analcite, clinoptilolite, chabazite et erionite.

10. La méthode selon l'une quelconque des revendications 1 à 9, selon laquelle l'ion ammonium est introduit dans la zéolithe en quantité de 0,5 à 15 % en poids.

11. La méthode selon l'une quelconque des revendications 1 à 10, selon laquelle l'ion ammonium est introduit dans la zéolithe en quantité de 1,5 à 5 % en poids.

12. La méthode selon l'une quelconque des revendications 7 à 11, selon laquelle l'ion argent est introduit dans la zéolithe en quantité de 0,1 à 15 % en poids, l'ion cuivre est introduit en quantité de 0,1 à 8 % en poids et l'ion zinc est introduit en quantité de 0,1 à 8 % en poids.

13. La méthode selon l'une quelconque des revendications 7 à 12, selon laquelle l'étape de remplacement de la totalité ou d'une partie des ions échangeables ioniquement dans la zéolithe est conduite en mettant en contact la zéolithe avec une solution mixte contenant outre les ions ammonium et argent, au moins un métal choisi dans le groupe comprenant les suivants : cuivre, zinc, mercure, étain, plomb, bismuth, cadmium, chrome et thallium.

14. La méthode selon l'une quelconque des revendications 7 à 12, selon laquelle l'étape de remplacement de la totalité ou d'une partie des ions échangeables ioniquement dans la zéolithe est conduite en mettant en contact la zéolithe avec des solutions séparées contenant chacune au moins un ion choisi dans le groupe comprenant les suivants : ammonium, argent, cuivre, zinc, mercure, étain, plomb, bismuth, cadmium, chrome et thallium.

15. Une méthode pour préparer une composition de résine antibiotique comprenant l'étape d'incorporation d'une zéolithe dans laquelle la totalité ou une partie des ions échangeables ioniquement est remplacée par des ions argent et ammonium dans la résine par pétrissage de la résine avec la zéolithe ou revêtement de la zéolithe sur la surface de la résine.

16. La méthode selon la revendication 15, selon laquelle une résine est employée qui est au moins un élément choisi dans le groupe comprenant les suivants : polyéthylène, polypropylène, chlorure de polyvinyle, résine ABS, nylons, polyesters, chlorure de polyvinylidène, polyamides, polystyrène, polyacétals, alcool polyvinylique, polycarbonate, résines acryliques, fluoroplastiques, élastomère de polyuréthanne, résines phénoliques, résines d'urée, résines de mélamine, résines de polyesters insaturés, résines époxy, résines d'uréthanne, rayonne, rayonne cuproammoniacale, acétates, triacétates, vinylidène, caoutchoucs naturels ou synthétiques.

17. La méthode selon la revendication 15 ou 16, selon laquelle la zéolithe antibiotique est introduite en quantité de 0,05 à 80 % en poids.

18. La méthode selon l'une quelconque des revendications 15 à 17, selon laquelle la zéolithe antibiotique est introduite en quantité de 0,1 à 80 % en poids.

19. La méthode selon l'une des revendications 15 à 18, selon laquelle la zéolithe antibiotique est incorporée en quantité de 0,1 à 3 % en poids.

20. La méthode selon l'une quelconque des revendications 15 à 19, selon laquelle une zéolithe comprenant en outre des ions d'au moins un métal choisi dans un groupe comprenant les suivants : cuivre, zinc, mercure, étain, plomb, bismuth, cadmium et thallium est incorporée.

21. La méthode selon l'une quelconque des revendications 15 à 20, selon laquelle une zéolithe contenant des ions ammonium en quantité de 0,5 à 15 % en poids est incorporée.

22. Une méthode selon l'une quelconque des revendications 20 à 21 selon laquelle une zéolithe contenant des ions argent en quantité de 0,1 à 15 % en poids, des ions cuivre en quantité de 0,1 à 8 % en poids et des ions zinc en quantité de 0,1 à 8 % en poids est incorporée.

23. La méthode selon l'une quelconque des revendications 15 à 22, selon laquelle une zéolithe est incorporée qui est préparée conformément à la méthode de l'une quelconque des revendications 1 à 14.

FIG. 1

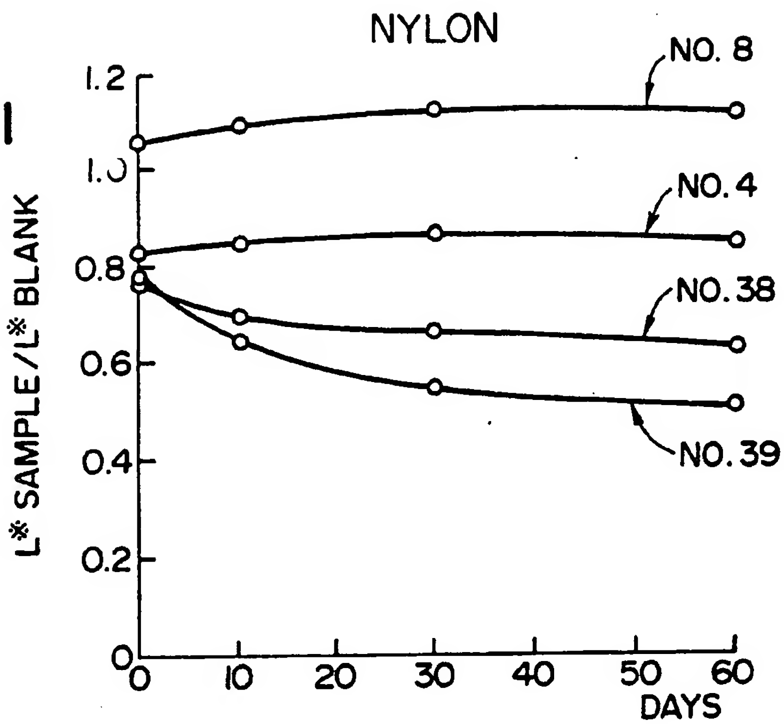

NYLON
NO. 8
NO. 4
NO. 38
NO. 39
L* SAMPLE / L* BLANK
1.2
1.0
0.8
0.6
0.4
0.2
0
0
10
20
30
40
50
60
DAYS

FIG. 2

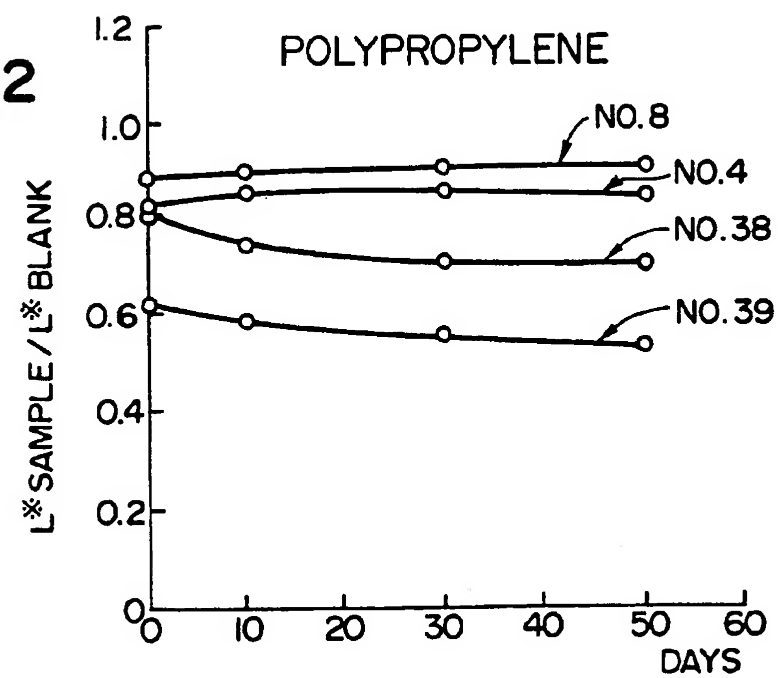

POLYPROPYLENE
NO. 8
NO. 4
NO. 38
NO. 39
L* SAMPLE / L* BLANK
1.2
1.0
0.8
0.6
0.4
0.2
0
0
10
20
30
40
50
60
DAYS

FIG. 3

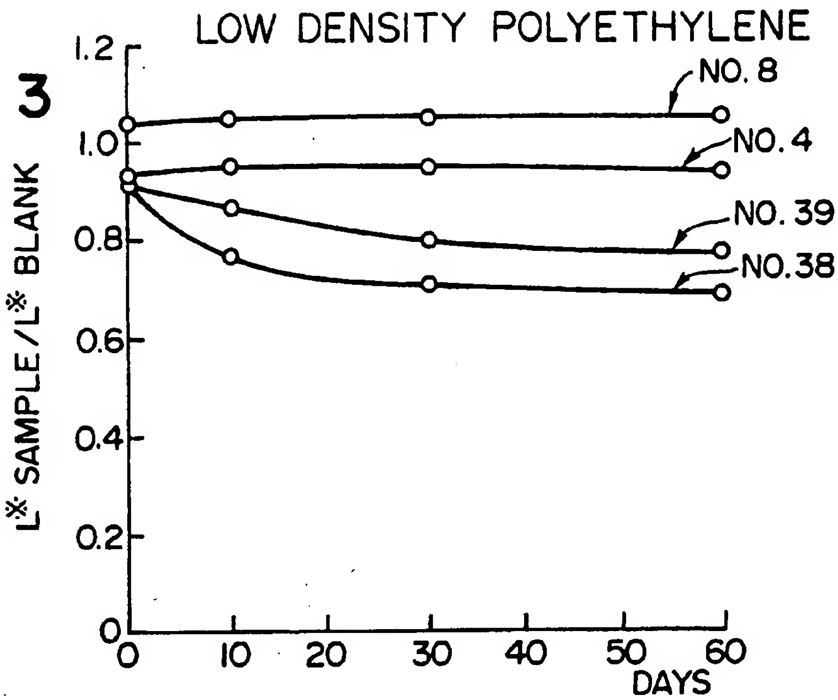

LOW DENSITY POLYETHYLENE
L* SAMPLE / L* BLANK
1.2
1.0
0.8
0.6
0.4
0.2
0
0
10
20
30
40
50
60
DAYS
NO. 8
NO. 4
NO. 39
NO. 38

FIG. 4

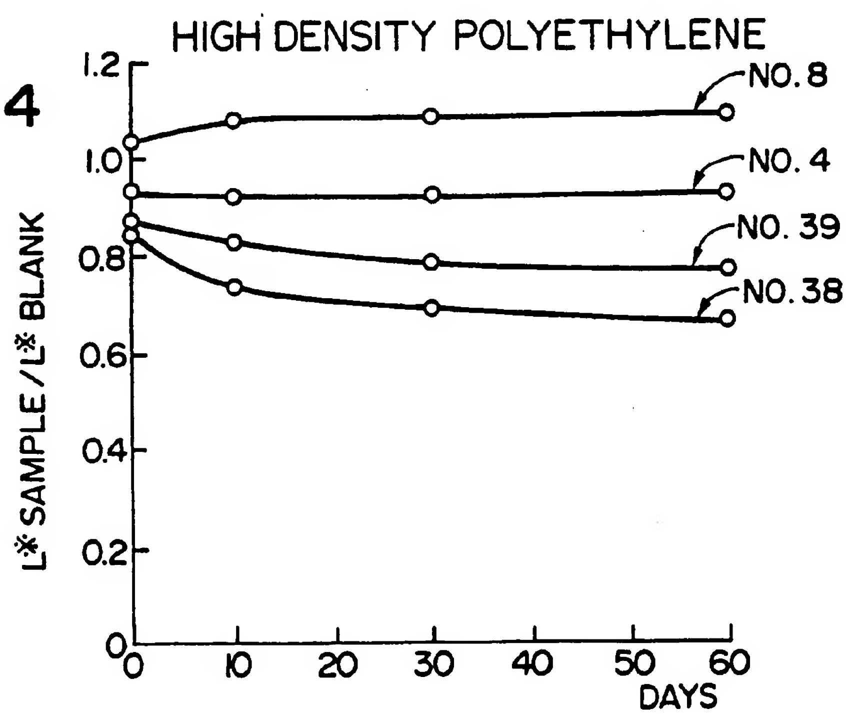

HIGH DENSITY POLYETHYLENE
L* SAMPLE / L* BLANK
1.2
1.0
0.8
0.6
0.4
0.2
0
0
10
20
30
40
50
60
DAYS
NO. 8
NO. 4
NO. 39
NO. 38

FIG. 5

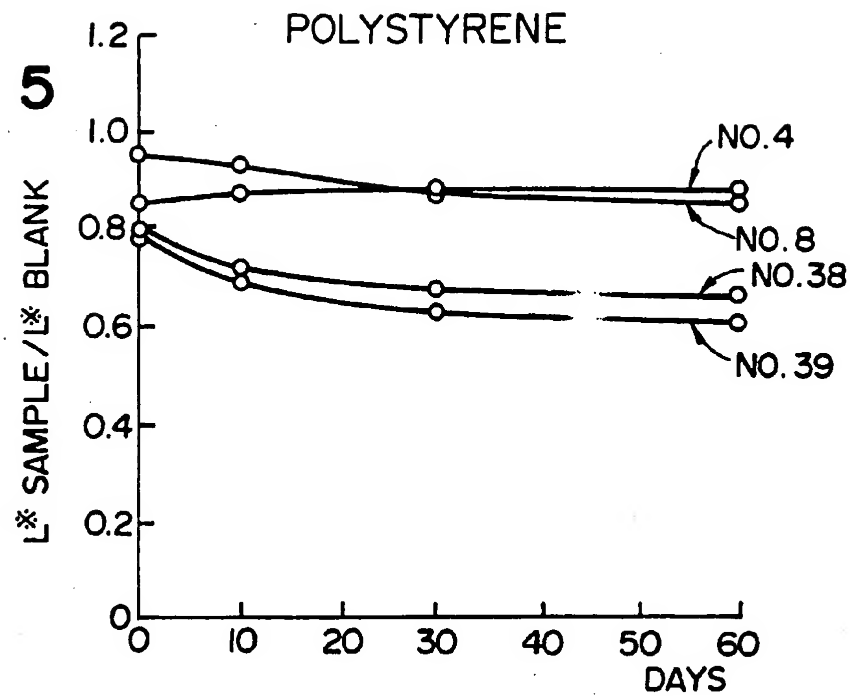

POLYSTYRENE
1.2
1.0
0.8
0.6
0.4
0.2
0
L* SAMPLE/L* BLANK
NO. 4
NO. 8
NO. 38
NO. 39
0
10
20
30
40
50
60
DAYS

FIG. 6

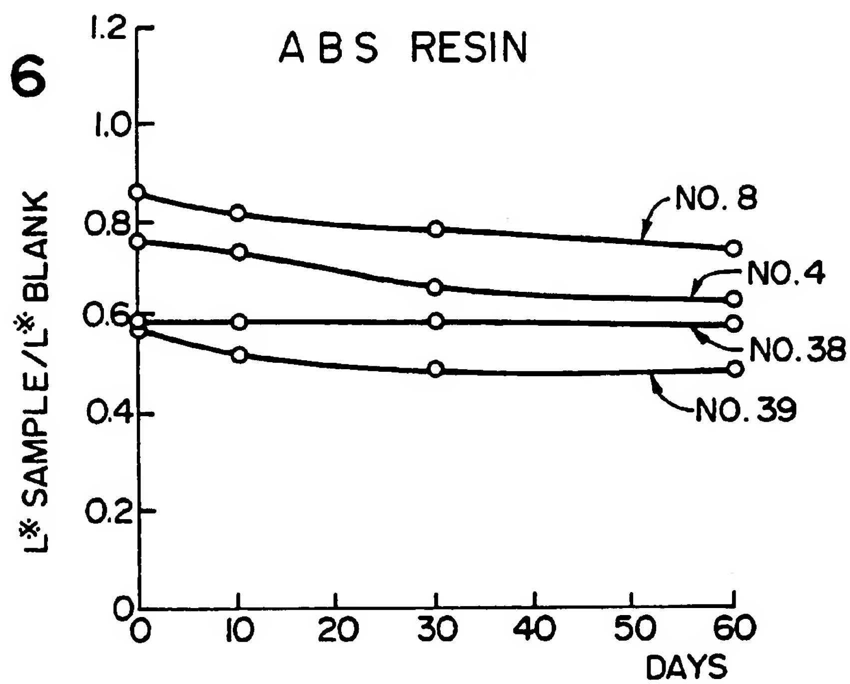
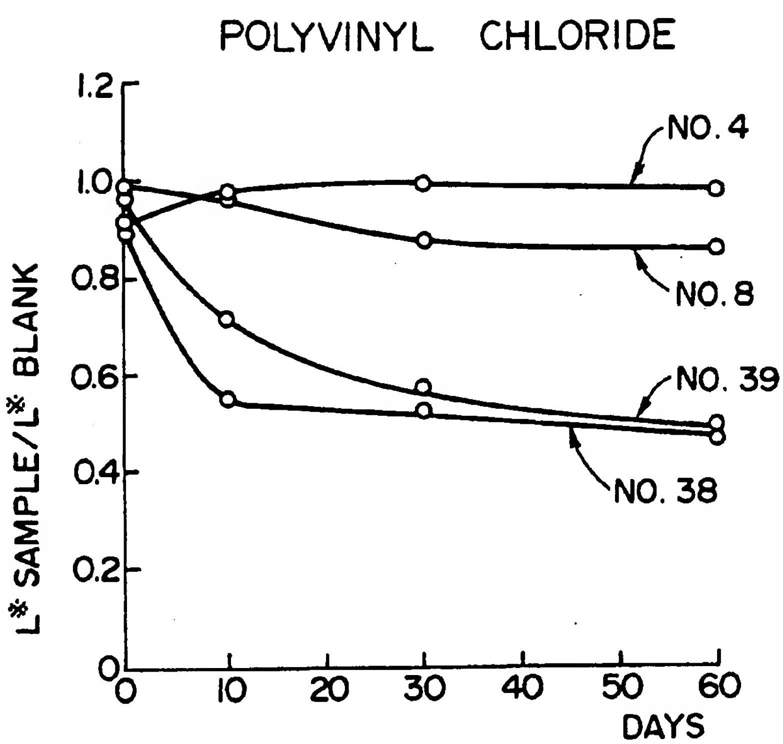

ABS RESIN
1.2
1.0
0.8
0.6
0.4
0.2
0
L* SAMPLE/L* BLANK
NO. 8
NO. 4
NO. 38
NO. 39
0
10
20
30
40
50
60
DAYS

FIG. 7


POLYVINYL CHLORIDE
L* SAMPLE/L* BLANK
1.2
1.0
0.8
0.6
0.4
0.2
0
0
10
20
30
40
50
60
DAYS
NO. 4
NO. 8
NO. 39
NO. 38